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High-Order Time-Dependent Perturbation Theory for Classical Mechanics and for Other Systems of First-Order Ordinary Differential Equations*

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A time-dependent perturbation solution is derived for a system of first-order nonlinear or linear ordinary differential equations. By means of an ansatz, justified *a posteriori*, the latter equations can be converted to an operator equation which is solvable by several methods. The solution is subsequently specialized to the case of classical mechanics. For the particular case of autonomous equations the solution reduces to a well-known one in the literature. However, when collision phenomena are treated and described in a classical "interaction representation" the differential equations are typically nonautonomous, and the more general solution is required. The perturbation expression is related to a quantum mechanical one and will be applied subsequently to semiclassical and classical treatments of collisions.

INTRODUCTION

Classical mechanics has been used extensively to treat experimental data on reactive collisions,[1] in part because exact calculations can be made. The corresponding exact quantum calculations in three dimensions are absent at present. Exact classical calculations of rotational–vibrational–translational energy transfer have also been useful.[2] The latter, in conjunction with classical approximations, provide insight into quantum approximations,[3] as do the several exact quantum results.[4]

In the present paper a "high-order" perturbation theory is developed in a form which gives final state properties in terms of integrals over initial state ones and so is suited to collision phenomena.[5] It permits systematic development of certain approximations in classical mechanics and, in conjunction with a correspondence principle for collisions,[6] permits an approximation of semiclassical matrix elements which occur in some collision problems.

In the present paper a perturbation theory is derived first for a system of ordinary differential equations more general than those characterizing classical mechanics and is later specialized to classical mechanics. In passing it may be noted that in a variation of constants treatment (e.g., of collisions in classical mechanics[7]) the differential equations for the "constants" are typically nonautonomous.

The first step in the over-all derivation is a conversion of the system of equations to an operator equation.[8] To this end an ansatz [Eq. (6)] will be introduced, one which is then justified *a posteriori*. The resulting operator equation can then be solved by one of several methods. Using one of these[9] we obtain Eqs. (6) and (15), and for classical mechanics Eqs. (24) and (26). [Using another method (iteration) one obtains instead (15′), while a time-ordered method yields instead (15″).]

Several applications of the present equations are given in subsequent articles.

PERTURBATION THEORY

The initial value problem for the system ($i=1,\cdots,n$) of differential equations, nonlinear or linear,

$$dx_i/dt=h_i(x,t)\equiv h_i^0(x,t)+h_i^1(x,t) \quad (t\geq t_0),$$
$$x_i=x_i^0 \quad (t=t_0), \quad (1)$$

is considered, where h_i^0 and h_i^1 are the unperturbed and perturbing terms; x denotes the totality of x_i's. We shall be mainly interested in applications where h_i^1 vanishes as $t\to t_0$ and as $t\to\infty$. This vanishing may occur either because of an explicit dependence of h_i^1 on t or, even when this dependence is absent, because of the range of x of interest[10] in the neighborhood of t_0 and $t=+\infty$.

Solution of the unperturbed problem yields constants of the motion $\bar{x}_i$. In the perturbed problem, when the above vanishing of h_i^1 occurs, these $\bar{x}_i$'s vary from their initial values at $t=t_0$ to final constant values at $t\sim\infty$. Transformation from x_i's to $\bar{x}_i$'s ("variation of constants") yields

$$d\bar{x}_i/dt=\bar{h}_i(\bar{x},t) \quad (t\geq t_0),$$
$$\bar{x}_i=\bar{x}_i^0 \quad (t=t_0), \quad (2)$$

where $\bar{h}_i$ vanishes when h_i^1 does and where $\bar{x}$ denotes the totality of $\bar{x}_i$'s. Even when (1) is autonomous (i.e., h_i depends on x alone), Eq. (2) is generally nonautonomous in collision phenomena, as noted earlier. In the case of classical mechanics Eq. (2) would form a classical counterpart of an "interaction representation" in quantum mechanics.[6] The ensuing results will apply to Eq. (2) and, when the barred symbols are replaced by unbarred ones, to Eq. (1) as well.

A first-order partial differential operator $D(t)$, acting on the space of functions of $\bar{x}$ and containing t as a parameter, can be defined[8]

$$D(t)=\sum_i \bar{h}_i(\bar{x},t)\,(\partial/\partial\bar{x}_i). \quad (3)$$

The system (2) can be rewritten as

$$df(\bar{x})/dt=D(t)f(\bar{x}) \quad (t\geq t_0),$$
$$\bar{x}_i=\bar{x}_i \quad (t=t_0), \quad (4)$$

where $f(\bar{x})$ is an arbitrary differentiable function of $\bar{x}$, since $df(\bar{x})/dt$ equals $\sum_i \partial f(\bar{x})/\partial\bar{x}_i(d\bar{x}_i/dt)$.

If the system (2) were autonomous, and $D(t)$ then written as D, the solution of (2) or (4) would be[8]

$$f(\bar{x})=[\{\exp[(t-t_0)D]\}f(\bar{x})]_{\bar{x}=\bar{x}^0}. \quad (5)$$

To treat the more general system (2) we seek instead a generalization of (5), and shall assume that $f(\bar{x})$ can be written as

$$f(\bar{x})=[\{\exp\mathcal{O}(t)\}f(\bar{x})]_{\bar{x}=\bar{x}^0}, \quad (6)$$

where $\mathcal{O}(t)$, like D, is to be a first-order partial differential operator. $\mathcal{O}(t)$ contains t as a parameter. Later, in Eq. (15), an explicit expression for this operator is given. For brevity $\exp\mathcal{O}(t)$ will be denoted by $\mathfrak{D}(t)$:

$$\mathfrak{D}(t)=\exp\mathcal{O}(t)=\sum_{n=0}^{\infty}\mathcal{O}^n(t)/n!. \quad (7)$$

Equations (4), (6) and (7) yield

$$df(\mathfrak{D}(t)\bar{x})/dt=D(t)f(\mathfrak{D}(t)\bar{x}) \quad \text{at} \quad \bar{x}=\bar{x}^0, \quad (8)$$

where d/dt acts only on the t in $\mathfrak{D}(t)$, because of the restriction $\bar{x}=\bar{x}^0$.

Because of the properties of the exponential of a first-order partial differential operator[11] one may write, for any function $g(\bar{x},t)$,

$$g(\mathfrak{D}(t)\bar{x},t)=\mathfrak{D}(t)g(\bar{x},t), \quad \text{at} \quad \bar{x}=\bar{x}^0. \quad (9)$$

Thus, (8) can be rewritten as

$$[d\mathfrak{D}(t)/dt]f(\bar{x})=\mathfrak{D}(t)D(t)f(\bar{x}), \quad \text{at} \quad \bar{x}=\bar{x}^0. \quad (10)$$

Omission of the arbitrary initial point $\bar{x}=\bar{x}^0$ and the arbitrary function $f(\bar{x})$ yields the operator equation

$$d\mathfrak{D}(t)/dt=\mathfrak{D}(t)D(t). \quad (11)$$

One form of solution[9] to a differential equation for an operator $U(t,t_0)$,

$$dU/dt=A(t)U, \qquad U(t_0,t_0)=1, \quad (12)$$

is

$$U(t,t_0)=\exp\mathfrak{B}(t,t_0), \quad (13a)$$

where[12]

$$\mathfrak{B}=\int_{t_0}^{t}A_{t_1}dt_1+\frac{1}{2}\int_{t_0}^{t}\left[A_{t_2},\int_{t_0}^{t_2}A_{t_1}dt_1\right]dt_2$$
$$+\frac{1}{4}\int_{t_0}^{t}\left[A_{t_3},\int_{t_0}^{t_3}\left[A_{t_2},\int_{t_0}^{t_2}A_{t_1}dt_1\right]dt_2\right]dt_3$$
$$+\frac{1}{12}\int_{t_0}^{t}\left[\left[A_{t_3},\int_{t_0}^{t_3}A_{t_2}dt_2\right],\int_{t_0}^{t_3}A_{t_1}dt_1\right]dt_3+\cdots. \quad (13b)$$

A_{t_i} denotes the operator $A(t_i)$, and $[\ ,\ ]$ denotes the commutator. Comparison of (11) and (12) shows that instead of (12) we need the equation satisfied by U^{-1}, the inverse of U:

$$dU^{-1}/dt=-U^{-1}A, \qquad U^{-1}(t_0,t_0)=1, \quad (14)$$

obtained by differentiation of $UU^{-1}=1$ and introduction of (12). Comparison of (14) with (11) shows that they are of the same form, but with U^{-1} and A replaced by $\mathfrak{D}$ and $-D$, respectively. Since the inverse of $\exp\mathcal{O}$ is $\exp(-\mathcal{O})$ one finds from (13) that the $\mathcal{O}$ in (6) is

given by

$$\mathcal{O}(t)=\int_{t_0}^{t}D_{t_1}dt_1-\frac{1}{2}\int_{t_0}^{t}\left[D_{t_2},\int_{t_0}^{t_2}D_{t_1}dt_1\right]dt_2$$
$$+\frac{1}{4}\int_{t_0}^{t}\left[D_{t_3},\int_{t_0}^{t_3}\left[D_{t_2},\int_{t_0}^{t_2}D_{t_1}dt_1\right]dt_2\right]dt_3$$
$$+\frac{1}{12}\int_{t_0}^{t}\left[\left[D_{t_3},\int_{t_0}^{t_3}D_{t_2}dt_2\right],\int_{t_0}^{t_3}D_{t_1}dt_1\right]dt_3+\cdots. \tag{15}$$

where each D_{t_i} denotes $D(t_i)$. Since the commutators of this D_{t_i} at various times t_i are, like D_{t_i} itself, first-order partial differential operators, $\mathcal{O}(t)$ is also, thus justifying *a posteriori* the ansatz (6). [Thus, by reversing the sequence of steps in the derivation one can verify that the solution given by (6) and (15) satisfies (2).]

Had (1) been used instead of (2), a solution identical with (6) and (15) would have been obtained but having x_i, x_i^0, and h_i's instead of $\bar{x}_i$, $\bar{x}_i^0$, and $\bar{h}_i$'s. (The restriction of h_i^1 need not be imposed then, except for possible convergence questions at large t. This point is returned to in a later section.) Solving the operator Eq. (11) could also have been based on time ordering or on simple iteration [cf. Refs. 13–15, or Eqs. (15′) and (15″) below].

When the system of differential equations (2) is autonomous, the commutators in (15) vanish since the D_{t_i}'s no longer depend on t_i. Equation (15) then reduces to the well-known result (5).

The ansatz (6), leading from (4) to (11), could undoubtedly be replaced by a more basic Lie-algebraic argument, a point to which we shall return in a later communication, $D(t)$ being an infinitesimal generator of a Lie algebra. However, the argument given earlier suffices for the immediate purpose. Again, the results (6) and (15), together with (24) and (26), may be known to workers in that field, but have not to our knowledge been published explicitly.

An iterative solution of (11) or (5) leads to a known[15] result for $f(\bar{x})$:

$$f(\bar{x})=[\mathfrak{O}(t)f(\bar{x})]_{\bar{x}=\bar{x}^0},$$

where

$$\mathfrak{O}(t)=1+\int_{t_0}^{t}D_{t_1}dt_1+\int_{t_0}^{t}\left(\int_{t_0}^{t_2}D_{t_1}D_{t_2}dt_1\right)dt_2$$
$$+\int_{t_0}^{t}\left[\int_{t_0}^{t_3}\left(\int_{t_0}^{t_2}D_{t_1}D_{t_2}D_{t_3}dt_1\right)dt_2\right]dt_3+\cdots, \tag{15′}$$

a result consistent (after some manipulation) with (7) and (15).

A time-ordered solution of (11) yields instead

$$f(\bar{x})=[\mathfrak{O}(t)f(\bar{x})]_{\bar{x}=\bar{x}^0},\quad \mathfrak{O}(t)=P\exp\int_{t_0}^{t}D_{t_1}dt_1, \tag{15″}$$

where P denotes the time-ordering operator.[16a]

APPLICATION TO CLASSICAL MECHANICS

The preceding solutions can be specialized now to the case where the independent variables occur in canonically conjugate pairs. The classical mechanical equations of motion for a system with generalized coordinates q_i, canonically conjugate momenta p_i, and Hamiltonian $H(q, p, t)$ are

$$dq_i/dt=\partial H/\partial p_i,\qquad dp/dt=-\partial H/\partial q_i. \tag{16}$$

(Throughout, q and p will denote the totality of q_i's and p_i's, respectively.)

The Hamiltonian is the sum of unperturbed and perturbed terms, H_0 and H_1:

$$H(q, p, t)=H_0(q, p, t)+H_1(q, p, t). \tag{17}$$

Transformation to new variables $\bar{q}_i$ and $\bar{p}_i$ which are constants of the motion of the unperturbed problem is conveniently made by means of a generating function $W(q, \bar{p}, t)$ satisfying the Hamilton–Jacobi[17] equation for the unperturbed problem,

$$H_0(q, p, t)+\partial W(q, \bar{p}, t)/\partial t=0. \tag{18}$$

The transformation equations are

$$q_i=\partial W/\partial\bar{p}_i,\qquad p_i=\partial W/\partial q_i. \tag{19}$$

The generating function W transforms H to a new Hamiltonian $\bar{H}(\bar{q}, \bar{p}, t)$,

$$\bar{H}(\bar{q}, \bar{p}, t)=H(q, p, t)+\partial W(q, \bar{p}, t)/\partial t, \tag{20a}$$

which in virtue of (17) and (18) becomes

$$\bar{H}(\bar{q}, \bar{p}, t)=H_1(q, p, t). \tag{20b}$$

[Thus, to obtain $\bar{H}$, the solutions $q(\bar{q}, \bar{p}, t)$ and $p(\bar{q}, \bar{p}, t)$ of the unperturbed problem are introduced into $H_1(q, p, t)$.] The new equations of motion are

$$d\bar{q}_i/dt=\partial\bar{H}(\bar{q}, \bar{p}, t)/\partial\bar{p}_i,$$
$$d\bar{p}_i/dt=-\partial\bar{H}(\bar{q}, \bar{p}, t)/\partial\bar{q}_i. \tag{21}$$

The operator $D(t)$, defined by (3), thus becomes[16b]

$$D(t)=-\{\bar{H}(t)\ ,\ \} \tag{22}$$

where $\{\ ,\ \}$ denotes the Poisson–Bracket:

$$\{X, Y\}=\sum_i(\partial X/\partial\bar{q}_i\partial Y/\partial\bar{p}_i-\partial X/\partial\bar{p}_i\partial Y/\partial\bar{q}_i). \tag{23}$$

The solution to (21) is

$$f(\bar{q}_i, \bar{p}_i)=[(\exp\mathcal{O})f(\bar{q}, \bar{p})]_{\bar{q}=\bar{q}^0,\bar{p}=\bar{p}^0} \tag{24}$$

for any function f of the $\bar{q}_i$'s and $\bar{p}_i$'s, where $\mathcal{O}$ is given by (15) and (22). If the iterative solution (15′) or time-ordered one (15″) were employed, $\exp\mathcal{O}$ would be given by $\mathfrak{O}$ in (15′) or (15″), respectively, where now (22) is introduced. When (15) is used instead, (26) is obtained, as follows.

Since D is now a Poisson–Bracket, Eq. (15) can first be simplified: One readily verifies that Jacobi's identity[18] for Poisson–Brackets can be rewritten in operator form as

$$[\mathbf{X}, \mathbf{Y}]=\{\{X, Y\},\ \}, \tag{25a}$$

where

$$\mathbf{X}=\{X,\ \}\quad\text{and}\quad\mathbf{Y}=\{Y,\ \}. \tag{25b}$$

Consequently, (15) becomes

$$\Theta=\{B,\ \},\tag{26a}$$

where

$$-B=\int_{t_0}^{t}\bar{H}_{t_1}dt_1+\frac{1}{2}\int_{t_0}^{t}\left[\bar{H}_{t_2},\int_{t_0}^{t_2}\bar{H}_{t_1}dt_1\right]dt_2 + \frac{1}{4}\int_{t_0}^{t}\left[\bar{H}_{t_3},\int_{t_0}^{t_3}\left[\bar{H}_{t_2},\int_{t_0}^{t_2}\bar{H}_{t_1}dt_1\right]dt_2\right]dt_3 + \frac{1}{12}\int_{t_0}^{t}\left[\left[\bar{H}_{t_3},\int_{t_0}^{t_3}\bar{H}_{t_2}dt_2\right],\int_{t_0}^{t_3}\bar{H}_{t_1}dt_1\right]dt_3+\cdots.\tag{26b}$$

We note that the symbol $\exp\{B,\ \}$ arising from (24) and (26a) represents

$$\exp\{B,\ \}=1+\{B,\ \}+(1/2!)\{B,\{B,\ \}\}+(1/3!)\{B,\{B,\{B,\ \}\}\}+\cdots.\tag{27}$$

The solution to (21) is given by (24) and (26). Had (1) been used instead of (2) as a starting point, (26) would again have been obtained, but with $\bar{q}$, $\bar{p}$, $\bar{q}^0$, $\bar{p}^0$, and $\bar{H}$ replaced by q, p, q^0, p^0, and H.

In some problems interest lies in the perturbation of variables c_i (e.g., the orbital elements in celestial mechanics[19]) which are functions of the canonically conjugate pairs, rather than the pairs themselves. Equations (24) and (26) can still be applied.[20]

An alternative derivation of (24) and (26), but not of (6) and (15), can be given[6] using a quantum mechanical expression and the correspondence between classical and quantum mechanics.

COMPARISON WITH PREVIOUS WORK

Grobner[8] has employed an operator formalism ("solution by Lie series"), particularly for the case that the system (1) is autonomous.[21] Solutions were made iteratively or by other[13] methods, though not employing Magnus' result. When the system of equations (1) is autonomous, D (with x's and h's instead of $\bar{x}$'s and $\bar{h}$'s) becomes the operator which enters into Lie's theory of ordinary differential equations.[22] An iterative solution for nonautonomous systems was noted previously.[15]

Operator methods were introduced into classical mechanics by Koopman.[23] A rather different operator formalism has been employed by Garrido[14] in a perturbation theory for classical mechanics. He noted that the operator Ω defined in

$$\frac{dF}{dt}=\Omega F\equiv\sum_i\left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i}-\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i}\right)F\tag{28}$$

is a linear differential operator and that, for that reason, the equation for the evolution of a function of phase space, $F(q,\ p)$, is equivalent to an operator equation[24]

$$dF/dt=[\Omega,F],\tag{29}$$

if F in (29) is reinterpreted in an operator acting on the space of functions of phase space. An automorphism was next tacitly assumed,[25] by analogy with a known quantum mechanical result, and a solution was obtained both in terms of a time-ordered product and iteratively (Magnus' method was not employed). Appealing to another analogy[26] between an ordinary and an operator equation, he obtained an expression for the time evolution of the *function* F. The present method of derivation of (15′) and (15″) can be regarded as providing a more rigorous derivation of his final results.[27]

Garrido's final equation has been applied to rotational–translational energy transfer in a plane.[28] Similarly, the present results can be applied to collision phenomena, either using the solutions (24) and (26) or using (15′) or (15″).

In the perturbation treatment of (1) or (2) we were particularly interested in the case where $h_i^1\longrightarrow 0$ as $t\longrightarrow\infty$. In problems such as forced harmonic oscillator

$$\dot{q}=p,\qquad \dot{p}=\omega_0^2q+a\sin\omega t,$$

where clearly $h_i^1\not\to 0$ as $t\longrightarrow\infty$, the series for $\Theta(t)$ terminates after the second term, and no difficulty arises. However, in problems such as the anharmonic oscillator

$$\dot{q}=p,\qquad \dot{p}=\omega^2q+aq^2,$$

secular terms develop. They can be avoided by resorting to other methods, such as Lindsted's procedure[29] or canonical perturbation theory.[30] In the latter theory, some old variables appear as a perturbation series in terms of the new. In collision problems on the other hand, one is much more interested in an expression for the new variables (i.e., the new constants of the motion) at $t\cong\infty$ in terms of the old, as for example in the solution given by (24) and (26).

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[5] This method may be contrasted with others. Surveys of other methods are given in (a) R. Bellman, *Perturbation*

Techniques in Mathematics, Physics and Engineering (Holt, Rinehart and Winston, Inc., New York, 1964); (b) W. F. Ames, *Nonlinear Ordinary Differential Equations in Transport Processes* (Academic Press Inc., New York, 1968); (c) *Differential Equations and Dynamical Systems*, J. K. Hale and J. P. LaSalle, Eds. (Academic Press Inc., New York, 1967).

[6] R. A. Marcus, J. Chem. Phys. (to be published).

[7] Compare A. O. Cohen and R. A. Marcus, J. Chem. Phys. **49,** 4509 (1968).

[8] E.g., W. Grobner, *Die Lie-Reihen und Ihre Anwendungen* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1967), 2nd ed. (autonomous systems); cf. K. T. Chen, Arch. Rat. Mech. Anal. **13,** 348 (1963), which came to our attention after submission of the present article. It contains a quite different derivation of (11), lengthier than the present though self-contained.

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[10] For example when (1) represents a system of equations of classical mechanical motion for a collision of two particles, h_i^1 reflects their interaction. In a conservative system neither h_i^0 nor h_i^1 depend explicitly on time t, but nevertheless h_i^1 vanishes as $t \to \pm\infty$, because in the usual collision problems the particles are then far apart. (t_0 is chosen to be any arbitrary time in the region where the initial interaction of the particles is negligible.)

[11] W. Grobner, Ref. 8, p. 17.

[12] In a related problem, coefficients of the Baker–Campbell–Hausdorff series have been calculated to a high order by computer [R. D. Richtmyer and S. Greenspan, Commun. Pure Appl. Math. **18,** 107 (1965).] Applications of Magnus' solution are given in D. W. Robinson, Helv. Phys. Acta **36,** 140 (1963); P. Pechukas and J. C. Light, J. Chem. Phys. **44,** 3897 (1966); S. Chan, J. C. Light and J. Lin, *ibid.* **49,** 86 (1968); E. H. Wichmann, J. Math. Phys. **2,** 876 (1961); R. M. Wilcox, *ibid.* **8,** 962 (1967) and references cited therein; M. Lutzky, *ibid.* **9,** 1125 (1968). Sometimes the third term of the series is written more symmetrically, but the present form, due to Magnus, emphasizes that the series terminates if A_{ti} and

$$\int_{t_0}^{t_i} A_{ti} dt_j$$

commute.

[13] E. H. Abate and F. Hofelich, Z. Physik **209,** 13 (1968).

[14] (a) L. M. Garrido, Proc. Phys. Soc. (London) **76,** 33 (1960); J. Math. Anal. Appl. **3,** 295 (1961); (b) L. M. Garrido and F. Gascon, Proc. Roy. Soc. (London) **81,** 1115 (1963).

[15] See, e.g., K. T. Chen, Ref. 8; J. Diff. Equations **2,** 438 (1966); for classical mechanics see L. M. Garrido and F. Gascon, Ref. 14, Eq. 12, a result discussed later.

[16] (a) For example E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), p. 464. (b) Thus, as seen from (21) D now becomes for the system (20), the "Liouville operator," defined, for example, in R. W. Zwanzig, in *Lectures in Theoretical Physics*, W. E. Brittin, B. W. Downs and J. Downs, Eds. (Interscience Publishers, Inc., New York, 1961), p. 107.

[17] (a) See, e.g., H. C. Corben and P. Stehle, *Classical Mechanics* (John Wiley & Sons, Inc., New York, 1960), 2nd ed., pp. 178, 184; (b) E. W. Brown and C. A. Shook, *Planetary Theory* (Cambridge University Press, London, 1933), p. 125.

[18] Reference 17(a), p. 221.

[19] See, e.g., T. E. Sterne, *An Introduction to Celestial Mechanics* (Interscience Publishers, Inc., New York, 1960), p. 100ff; S. W. Groesberg, *Advanced Mechanics* (John Wiley & Sons, Inc., New York, 1968), p. 306ff.

[20] Since the c_i^0 are functions of the q^0's and p^0's, (24) and (26) yield c_i equal to $\exp\{B, \quad\}c_i^0$. Finally, the chain rule for differentiation converts $\{B, \quad\}$ to $\sum_{k,j}\{c_k^0, c_j^0\}(\partial B/\partial c_k^0)(\partial/c_j^0)$.

[21] Nonautonomous systems were considered by adjoining t to the set of dependent variables. [See, however, G. R. Sell, in Ref. 5(c), p. 531.] In our case the use of this device would have destroyed the similarity of classical and (the customary) quantum equations used elsewhere in applications.

[22] See, e.g., R. Hermann, *Differential Geometry and the Calculus of Variations* (Academic Press Inc., New York, 1968), Chap. 6; E. L. Ince, *Ordinary Differential Equations* (Dover Publications, Inc., New York, 1956), Chap. IV.

[23] B. O. Koopman, Proc. Nat. Acad. Sci. **17,** 315 (1931); cf. J. von Neumann, Ann. Math. **33,** 587 (1932); E. H. Wichmann, Ref. 12.

[24] Reference 14(b), Eq. (5).

[25] Compare assumption of Eqs. (6) and (7) in Ref. 14(b) whose analog in our case would be our ansatz (6), leading to the automorphism represented by our (9).

[26] Analogy was made by comparison of Eq. (3) of Ref. 14(b) with the "operator equation" there, Eq. (2).

[27] See also Ref. 6, which treats what we have termed there the "interaction" and "mixed-interaction" pictures (or representations) in classical mechanics. In Ref. 14 the first is used, while in the present paper the second is employed, it being the standard one in classical mechanics. Both pictures are treated and compared in Ref. 6.

[28] F. J. Zeleznik, J. Chem. Phys. **47,** 3410 (1967).

[29] Reference 5(a), p. 57.

[30] See, e.g., D. Ter Haar, *Elements of Hamiltonian Mechanics* (North-Holland Publishing Company, Amsterdam, 1961), p. 153; Ref. 17(a), p. 251ff.

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Calculation of Transition Probabilities for Collinear Atom–Diatom and Diatom–Diatom Collisions with Lennard-Jones Interaction

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Numerical integration of the close coupled scattering equations is performed to obtain vibrational transition probabilities for three models of the electronically adiabatic H_2–H_2 collision. All three models use a Lennard-Jones interaction potential between the nearest atoms in the collision partners. The results are analyzed for some insight into the vibrational excitation process, including the effects of anharmonicities in the molecular vibration and of the internal structure (or lack of it) in one of the molecules. Conclusions are drawn on the value of similar model calculations. Among them is the conclusion that the replacement of earlier and simpler models of the interaction potential by the Lennard-Jones potential adds very little realism for all the complication it introduces.

INTRODUCTION

There is current interest in quantum-mechanical treatments of molecular collisions involving excitation of internal degrees of freedom and possibly reaction. The collision systems pose a multichannel scattering problem, commonly solved by the coupled channels (CC) method. The CC equations are coupled differen-